EUROPEAN PATENT APPLICATION

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(54) **Secondary ion mass spectrometric analysis of metals and method of preparing standard sample therefor.**

(57) A method of analyzing a solid, metal-containing sample by secondary ion mass spectrometry for the determination of the concentration of the metal, wherein the sample is shaped into a disc and measured for the metal ion intensity of secondary ion mass spectrometry. The disc is prepared by a process including the steps of: (a) mixing the sample with a liquid to dissolve the metal; (b) separating the metal from the solution as solids to form a first solid mass containing the metal; (c) calcining the solid mass to convert the metal into an oxide and to obtain a second solid mass; (d) mixing the second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of the metal oxide to obtain a mixture having a particle size of not greater than 100 μm; and (e) shaping the mixture into the disc. When the sample is a liquid, the steps (a) and (b) are omitted. This technique is applicable for the preparation of a standard sample having a known composition of metals used for constructing a calibration curve.

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This invention relates to a method of analyzing a metal-containing sample for the determination of the concentration of the metal by secondary ion mass spectrometry and to a method of preparing a standard sample for use in such a secondary ion mass spectrometric analysis.

Ion mass spectrometric analysis has been applied to a variety of solid materials such as films, metals and dusts. In this technique, a sample is bombarded with an ion beam of, for example, 5-15 KeV Ar^+, to cause neutral atoms and ions to be ejected from the sample. The positive ions are extracted into a mass spectrometer and analyzed. Details of this technique are disclosed in, for example, Morrison, G. H. et al, Analytical Chemistry, 47, 933 (1975) and Ishizuka, T., Analytical Chemistry, 46, 1487 (1974).

The conventional method using the secondary ion mass spectrometry has a problem because it cannot be applicable for the analysis of an insulating sample. While incorporation of carbon into the sample could solve the problem of static charging, another problem would arise because the carbon adversely affects the resolution of the mass spectrum. The conventional method poses a further problem because the intensity of the secondary ion varies when the sample is not homogeneous. This will be easily appreciated since the sample is bombarded with a microbeam.

In order to obtain exact quantitative analytical data by secondary ion mass spectrometric analysis, it is necessary to prepare a calibration curve using a standard sample having a known composition. No satisfactory method is, however, known in the art which can prepare a desired standard sample matching a sample to be measured.

The present invention has been made to solve the above problems.

There is provided in accordance with one aspect of the present invention a method of analyzing a solid, metal-containing material by secondary ion mass spectrometry for the determination of the concentration of the metal, comprising the steps of processing the metal-containing material into a disc, and subjecting said disc to a secondary ion mass spectrometric analysis, characterized in that said processing step includes the sub-steps of:

(a) mixing said metal-containing material with a liquid to dissolve said metal in said liquid and to obtain a solution containing said metal;

(b) separating said metal from said solution as solids to obtain a first solid mass containing said metal;

(c) calcining said first solid mass to convert said metal into an oxide of said metal and to obtain a second solid mass;

(d) mixing said second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of said metal oxide to obtain a mixture having a particle size of not greater than 100 μm; and

(e) shaping said mixture into said disc.

In another aspect, the present invention provides a method of analyzing a metal-containing liquid by secondary ion mass spectrometry for the determination of the concentration of the metal, comprising the steps of processing the metal-containing liquid into a solid disc, and subjecting said disc to a secondary ion mass spectrometric analysis, characterized in that said processing step includes the sub-steps of:

(a) separating said metal from said liquid as solids to obtain a first solid mass containing said metal;

(b) calcining said first solid mass to convert said metal into an oxide of said metal and to obtain a second solid mass;

(c) mixing said second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of said metal oxide to obtain a mixture having a particle size of not greater than 100 μm; and

(d) shaping said mixture into said disc.

The present invention further provides a method of preparing a standard sample for use in secondary ion mass spectrometric analysis, comprising the steps of:

(a) providing a solution of a first, reference metal and at least one second metal having a predetermined composition;

(b) separating said first and second metals from said solution as solids to obtain a first solid mass containing said first and second metals;

(c) calcining said first solid mass to convert said first and second metals into oxides and to obtain a second solid mass;

(d) mixing said second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of a total of said oxides of said first and second metals to obtain a mixture having a particle size of not greater than 100 μm; and

(e) shaping said mixture into a disc.

The present invention will now be described in detail below with reference to the accompanying drawings, in which:

Fig. 1 is a calibration curve prepared using a standard sample obtained in Example 1 and showing a relationship between the ion intensity ratio ($^{48}Ti^+/^{56}Fe^+$) and the concentration of Ti based on Fe; and

Fig. 2 is a calibration curve prepared using a standard sample obtained in Example 1 and showing a relationship between the ion intensity ratio ($^{51}V^+/^{56}Fe^+$) and the concentration of V based on Fe.

The present invention is directed to a method of the quantitative analysis of a metal-containing material by using a secondary ion mass spectrometer. Any commercially available ion micro analyzer (or ion
5 microprobe mass analyzer) may be suitably used for the purpose of the present invention. Examples of such analyzers include Hitachi Ion Micro Analyzer (Hitachi Co., Ltd., Japan), The GCA Ion Microprobe Analytical Mass Spectrometer (GCA Technology Division, USA) and CAMECA IMS Ion microscope (CAMECA Inc., France).

When the sample to be measured is a solid, metal-containing material, the sample is first mixed with a
10 suitable liquid to dissolve the metal and to obtain a solution containing the dissolved metal. The metal in the sample may be in the form of an elemental metal or a metal compound. The liquid to be used for the dissolution of the metal may be, for example, an aqueous acid solution such as nitric acid or hydrochloric acid. Except silver, any metal may be analyzed in accordance with the method of this invention. Examples of such metals include Fe, Mn, Ti, V, Cr, Cu, Ni, Sn, Ga, Ta, Al, Zr, rare earth elements and mixtures two or
15 more thereof.

The metal dissolved in the solution is then separated therefrom as solids. Various method may be adopted for the solidification and separation of the metal. For example, when the solution is an aqueous acid solution, the separation of the metal may be suitably performed by neutralizing the solution with an alkali such as sodium hydroxide, potassium hydroxide or ammonia to precipitate the metal as a hydroxide
20 and, thereafter, separating the precipitates by, for example, filtration. Alternatively, an organic reagent such as oxine may be used for the precipitation of the dissolved metal as a metal complex. Further, evaporation of the solution to dryness can give the solidified metal.

The thus separated solidified metal component (first solid mass) is then calcined at a temperature sufficient to convert the metal component into an oxide of the metal, preferably at 250-350 °C, thereby
25 obtaining a second solid mass. If necessary, the calcination of the first solid mass is preceded by drying at, for example, 80-150 °C.

The second solid mass is ground into particles having a particle size of not greater than 100 μm, preferably not greater than 80 μm, and mixed with silver powder having a particle size of not greater than 100 μm, preferably not greater than 80 μm. The amount of the silver powder is 0.15-5 parts by weight,
30 preferably 0.3-2 parts by weight, per part by weight of the metal oxide. It is convenient to pulverize the second solid mass together with commercially available silver powder with an average particle size of, for example, 30-80 μm into a particle size of 100 μm or less.

The resulting admixture is then shaped into a disc by any suitable known method, such as by press-molding at 100-400 kg/cm^2. The disc is mounted on a holder of an ion microanalyzer and is bombarded
35 with a microbeam in any suitable known manner.

When the sample to be measured is a liquid, metal-containing material, the sample is first processed to separate the metal as solids. This can be performed in the same manner as the above. The separated solids (first solid mass) are then dried, calcined, admixed with silver powder and shaped into a disc, in the same manner as above.

40 The above technique can be applied for the preparation of standard samples used for preparing calibration curves. Thus, a solution of a first, reference metal (M_1) and a second metal (M_2) having a predetermined composition is first prepared. The solution is then processed to separate the first and second metals as solids. This can be performed in the same manner as the above. The separated solids (first solid mass) are then dried, calcined, admixed with silver powder and shaped into a disc, in the same manner as
45 above, thereby obtaining the desired standard sample having known composition of the metals M_1 and M_2. In this case, it is advantageous to prepare a standard sample containing one standard metal and a plurality of metals having known composition.

By preparing various standard samples with different compositions and by analyzing these samples with the secondary ion mass spectrometer, a calibration curve representing a relationship between an ion
50 intensity ratio (M_2^+/M_1^+) and a relative concentration of M_2 in M_1 can be obtained. Using the thus prepared calibration curve, the concentration of metal M_2 in a sample containing metals M_1 and M_2 can be determined according to the method of the present invention. In this case, the concentration of the reference metal M_1 should be determined by another method such as ICP-AES (inductively coupled plasma-atomic emission spectrometry).

55 When the sample to be measured contains Fe, it is recommendable to use Fe as the reference metal for the standard samples. However, any metal may be used as the reference metal of standard samples, irrespective of whether or not the metal is contained in the sample to be measured. For example, Y (yttrium) may be used as the reference metal of standard samples for the analysis of yttrium-free samples.

In this case, the reference metal should be incorporated as an internal standard into the samples to be measured.

The following examples will further illustrate the present invention.

Example 1

Dust sample obtained from a dust separator of an iron sintering furnace was analyzed for the amounts of Mn, Ti, V and Cr according to the method of the present invention. The dust sample was first analyzed by ICP-AES to reveal that the iron content was 42 % by weight.

Preparation of Standard Samples:

Metallic iron was dissolved in hydrochloric acid to obtain an aqueous stock solution having an iron content of 1 % by weight (as elementary iron). A quantity of a second metal M_2 (Mn, Ti, V or Cr) was dissolved in 10 ml of the stock solution. The resulting second metal-containing solution was admixed with an aqueous sodium hydroxide solution to a pH of in the range of 9-11 to coprecipitate the second metal M_2 together with Fe as hydroxides. The precipitates were filtered and calcined at about 300 °C in an electric oven. The calcined product in the form of oxides was pulverized into a particle size of 74 μm or less and mixed with the same amount of metallic silver powder (average particle size of 43 μm). The mixture was press-molded in a die at about 200 kg/cm² to obtain a disc. The above procedure was repeated in the same manner as described with various amounts of respective second metals.

Construction of Calibration Curves:

The thus prepared standard samples were subjected to secondary ion mass spectrometry using Ion Microanalyzer IMA-2 (manufactured by Hitachi Ltd.) to measure the ion intensities M_2^+ and Fe^+. The ratios M_2^+/Fe^+ were plotted against the concentrations of M_2 (% by weight) based on Fe to form calibration curves. Figs. 1 and 2 illustrates the calibration curves of Ti and V, respectively.

At a signal to noise ratio (S/N ratio) of 2, the detection limits of Ti and V were found to be 0.4 ppm and 0.9 ppm, respectively, in terms of the content based on the weight of Fe.

The operating conditions of the ion microanalyzer were as follows:

Primary ion:	Ar^+
Primary ion accelerating potential:	12 kV
Primary ion current:	1-5 μA
Primary ion beam spot diameter	800 μm
Degree of vacuum:	2.7-6.7 x 10⁻⁵ Pa
Slit:	0.5 mm
Multiplier voltage:	1.4 kV

Reproducibility Tests:

A number of similar standard samples were prepared and measured for ion intensities. The standard variation of the ion intensities was as summarized in Table 1 below.

Table 1

Concentration of Second Metal Relative To Iron (μg/g)	Standard Variation (%)	
	Ti	V
1,000	1.2	1.5
3,000	0.82	0.84
10,000	0.24	0.56

The above standard samples were again measured on a different day on a different place. The standard variation of the ion intensities was as summarized in Table 2 below.

Table 2

Concentration of Second Metal Relative To Iron (μg/g)	Standard Variation (%)	
	Ti	V
1,000	0.98	1.1
3,000	0.38	0.59
10,000	0.23	0.48

Analysis of Dust Sample:

The dust sample was dissolved in a hydrochloric acid/hydrogen peroxide mixed solution and neutralized with an aqueous sodium hydroxide solution. The precipitates are calcined, mixed with Ag powder and shaped into a tablet in the same manner as that in the preparation of the standard samples. The disc was analyzed on the ion microanalyzer to measure ion intensities M_2^+. Based on the M_2^+/Fe^+ value, the concentration of M_2 was determined from the calibration curves. The results are shown in Table 3 together with those determined by ICP-AES.

Table 3

Metal	Secondary Ion Mass Spectrometry of the Present Invention (based on Fe)	ICP-AES (based on Fe)
Fe	-	42 %
Mn	0.62 %	0.59 %
Ti	0.52 %	0.54 %
V	510 ppm	420 ppm
Cr	60 ppm	50 ppm

Example 2

Preparation of Standard Samples:

Predetermined amounts (0.05 and 0.1 % by weight based on Fe) of Ti, Cr and Mn (as second metals) were dissolved in the stock solution prepared in Example 1. The resulting solution containing Fe, Ti, Cr and Mn was admixed with an aqueous sodium hydroxide solution to a pH of in the range of 9-11 to coprecipitate these metals as hydroxides. The precipitates were processed, mixed with Ag and shaped into a disc in the same manner as that of Example 1 to obtain two standard samples of a four components system. Above procedures were repeated in the same manner as described except that Ti, Cr and Mn were separately dissolved in the stock solution, thereby obtaining six standard samples of a two components system.

Secondary Ion Mass Spectrometry:

Each of the standard samples was then measured for the relative ion intensity ($M_2^+/^{56}Fe^+$). The results are summarized in Table 4.

Table 4

Second Metal	Concentration of Second Metal Based on Fe (% by weight)	Relative Ion Intensity ($\times 10^{-3}$) Two Components Four Components System System	
		Two Components System	Four Components System
Ti	0.05	5.6	5.2
Ti	0.1	10.8	10.6
Cr	0.05	4.1	3.9
Cr	0.1	8.3	8.0
Mn	0.05	3.2	3.1
Mn	0.1	6.0	6.0

The results shown in Table 4 indicate that the presence of other metals in the standard samples of the four components system has little influence upon the ion intensities ratios. In the foregoing examples, bombardment with O_2^+ was found to give the same analytical results.

Claims

1. A method of analyzing a solid, metal-containing material by secondary ion mass spectrometry for the determination of the concentration of the metal, comprising the steps of processing the metal-containing material into a disc, and subjecting said disc to a secondary ion mass spectrometric analysis, characterized in that said processing step includes the sub-steps of:

(a) mixing said material with a liquid to dissolve said metal in said liquid and to obtain a solution containing said metal;

(b) separating said metal from said solution as solids to form a first solid mass containing said metal;

(c) calcining said solid mass to convert said metal into an oxide of said metal and to obtain a second solid mass;

(d) mixing said second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of said metal oxide to obtain a mixture having a particle size of not greater than 100 μm; and

(e) shaping said mixture into said disc.

2. A method of analyzing a metal-containing liquid by secondary ion mass spectrometry for the determination of the concentration of the metal, comprising the steps of processing the metal-containing liquid into a solid disc, and subjecting said disc to a secondary ion mass spectrometric analysis, characterized in that said processing step includes the sub-steps of:

(a) separating said metal as solids from said liquid to form a first solid mass containing said metal;

(b) calcining said solid mass to convert said metal into an oxide of said metal and to obtain a second solid mass;

(c) mixing said second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of said metal oxide to obtain a mixture having a particle size of not greater than 100 μm; and

(d) shaping said mixture into said disc.

3. A method of preparing a standard sample for use in secondary ion mass spectrometric analysis, comprising the steps of:

(a) providing a solution of a first, reference metal and at least one second metal having a predetermined composition;

(b) separating said first and second metals from said solution as solids to obtain a first solid mass containing said first and second metals;

(c) calcining said first solid mass to convert said first and second metals into oxides and to obtain a second solid mass;

(d) mixing said second solid mass with silver powder in an amount of 0.15-5 parts by weight per part by weight of a total of said oxides of said first and second metals to obtain a mixture having a particle size of not greater than 100 μm; and
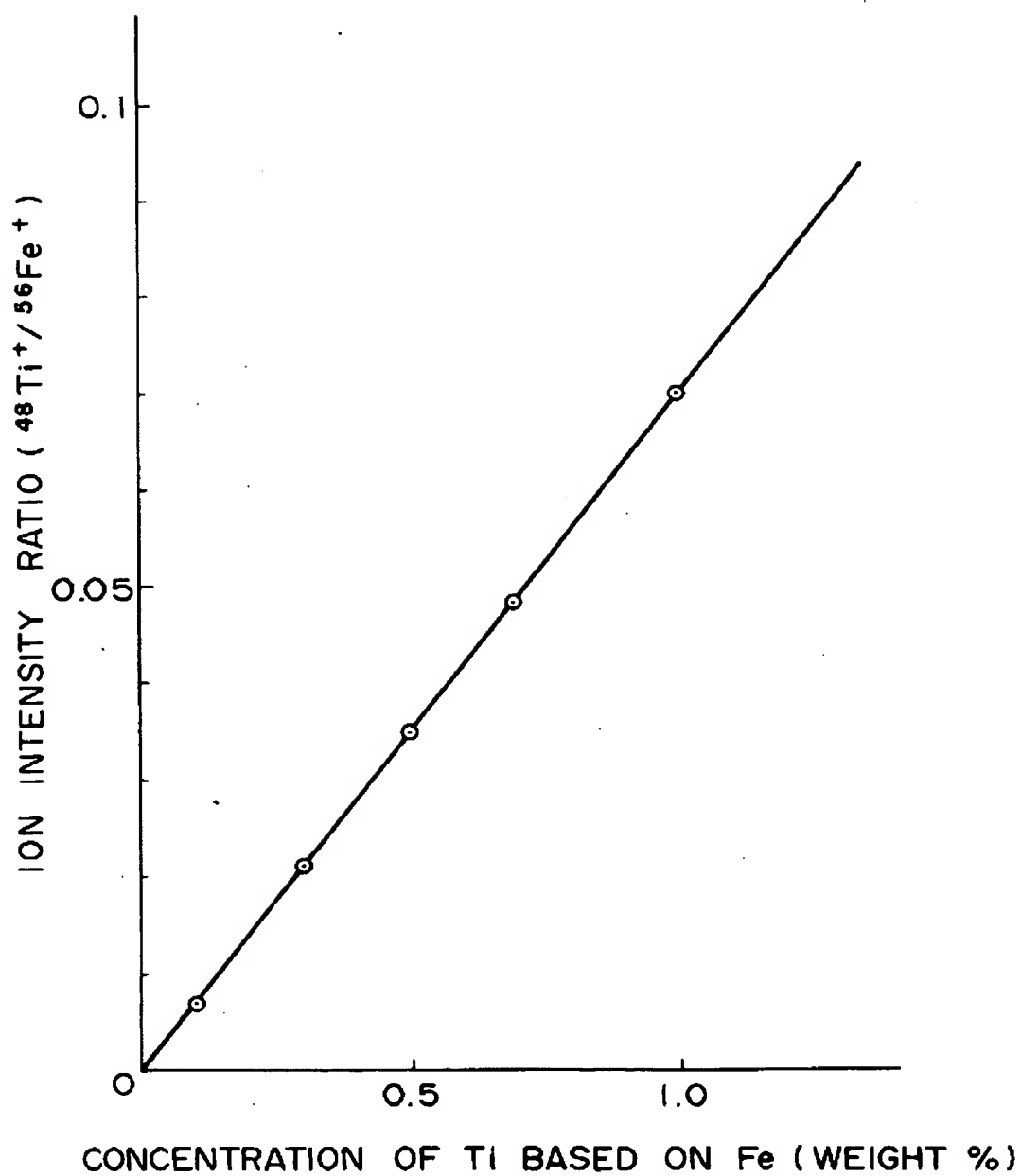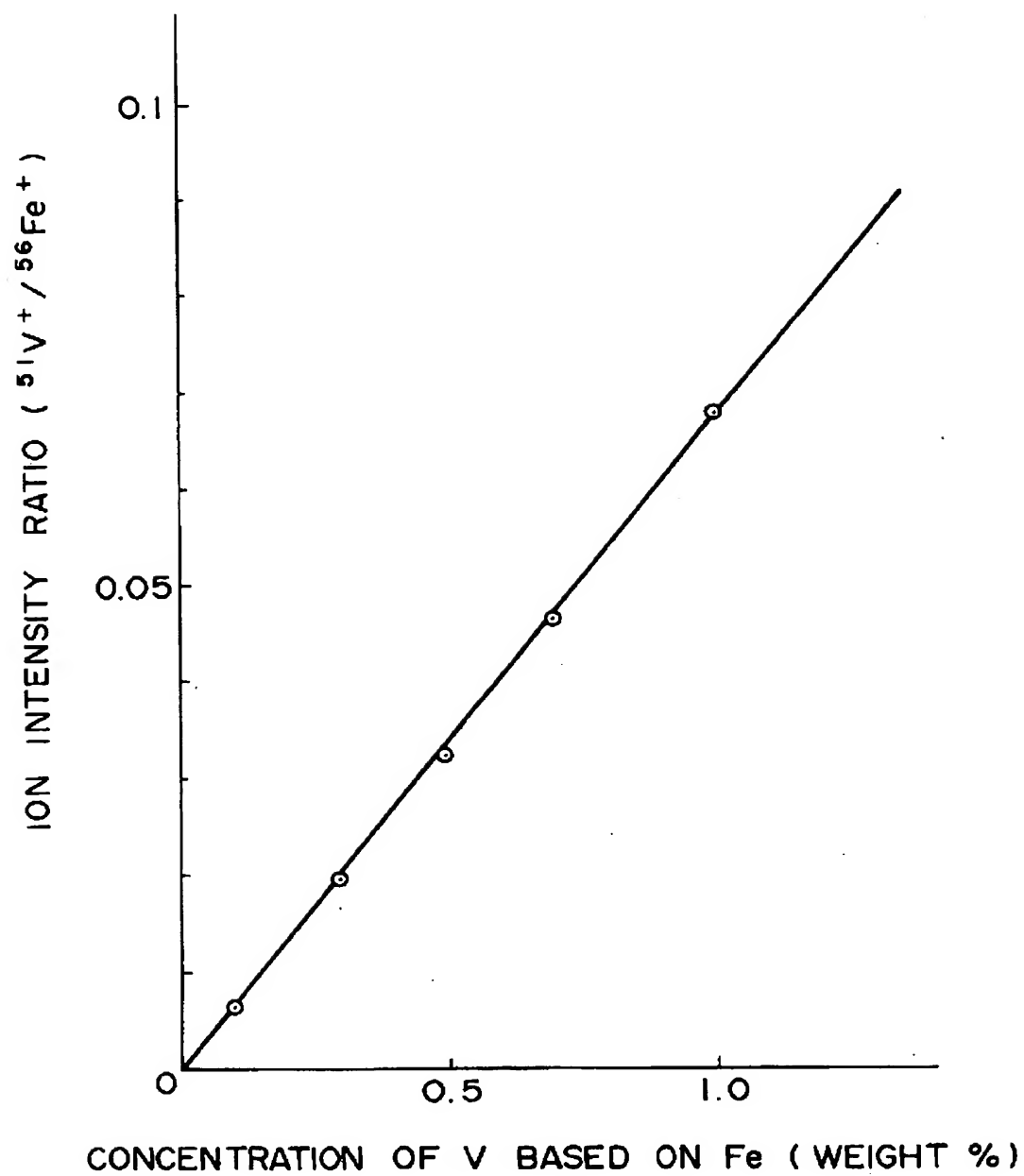
(e) shaping said mixture into a disc.

F I G. 1

F I G. 2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,A	ANALYTICAL CHEMISTRY vol. 46, no. 11 , September 1974 pages 1487 - 1491 T. ISHIZUKA 'Secondary ion mass spectrometry of rare earth elements' * page 1487, right column, paragraph 3 - page 1488, right column, paragraph 2; figure 1 * ---	1-3	G01N1/28
A	US-A-5 081 352 (MAKLAE ET AL.) * abstract; claims; figures * ---	1-3	
A	DATABASE WPI Week 8505, Derwent Publications Ltd., London, GB; AN 85-30609 & SU-A-1 101 714 (AGRIC AGROCHEM SERV) 7 July 1984 * abstract * ---	1-3	
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 265 (P-318)5 December 1984 & JP-A-59 132 344 (SUMITOMO) 30 July 1984 * abstract * ---	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.5) G01N H01J
A	DATABASE WPI Week 8436, Derwent Publications Ltd., London, GB; AN 84-222745 & JP-A-59 132 344 (SUMITOMO) 30 July 1984 * abstract * -----	1-3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 March 1994	Lipp, G